In-situ Deposition of Copper Oxide for Imparting Multifunctional Properties in Cotton Fabrics

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Abstract
In this study, a novel cost effective method of imparting multifunctional properties in cotton fabric has been developed. The in-situ deposition of copper oxide took place on fabric using copper sulphate pentahydrate ($CuSO_4.5H_2O$) as precursor of copper oxide.
The treated fabric was characterized with the help of FESEM to examine the change in morphology of fabric surface on deposition of copper oxide. Inductively Coupled Plasma- Mass Spectroscopy (ICP-MS) analysis was carried out to measure the amount of copper (Cu) present in fabric after treatment. The prepared samples were evaluated with respect to their UV protection property and antibacterial activity.
The study demonstrates that the chemical reduction method used to deposit the thin coating of copper oxide on cotton is uniformly distributed. The prepared sample could be able to exhibit an excellent UV protection property and a wash durable antibacterial activity which does not lose its effectiveness even after 5 washes. Other important physical parameters like tensile strength, air permeability and crease recovery were also examined to compare their results with respect to the untreated fabric. The experimental results show that no adverse change was apparently observed in the physical properties of the fabric after such treatment.

Keywords: *antibacterial activity, chemical reduction method, in-situ deposition, thin coating, UV protection*

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1. Introduction

For quality conscious customers, the manufacturers are nowadays exploring high value added products with multifunctional properties [1]. Traditionally, organic chemicals and finishes are being used for imparting various functionalities to the textiles. To name a few, antimicrobial, UV protection, water repellency and flame retardency have their own commercial importance [2,3]. But most of the times, these finishes suffer from poor wash durability. Due to their poor affinity with the textile substrate, these finishes leach out in the subsequent washes, which results in huge environmental pollution also [4]. Therefore, in recent times focus has shifted to inorganic materials, typically metal salts and oxides to impart some functional properties [5-7].

Application of inorganic materials opens up a new opportunity to develop multi-functionality in textiles. These inorganic materials are generally nontoxic and chemically stable under exposure to both high temperature and adverse weather conditions [8]. Due to the excellent chemical stability, non-toxicity and cost-effectiveness, these materials are now replacing the traditional organic compounds in various applications [9].

Among textile grade materials, cotton is popularly used in apparel grade applications due to its various merits. But cotton fabrics lack in providing good bacterial resistance and protection against UV radiations, unless given suitable treatments [10,11].

Recently, in-situ development of metal oxide nanoparticles on textile substrates has gained lot of popularity. This in-situ development of coating on fabric surface is carried out using a suitable precursor [12]. This bottom up approach can be useful in development of a wash durable, uniform and thin coating of metal oxides on textile substrates. Copper and its oxides are widely known to act as a broad spectrum biocide. They exhibit effective growth inhibition of bacteria, fungus, and algae [13,14]. Unlike the popular metal based antibacterial agent silver, copper and its oxides are cost effective and safe also [15]. In a study, coating of copper on polyester/silk blended fabric was performed using plasma sputtering method. In this way, antibacterial properties were introduced in the fabric. Although this process is eco-friendly, it is not cost-effective [16]. In another work, coating of copper was done on cotton to impart electromagnetic shielding. In this method, the fabric was initially soaked in copper sulphate solution followed by reduction in sodium hydrosulphite [17].

In the present study, attempt has been made to deposit copper oxide on cotton fabric. The in-situ deposition of copper oxide not only imparts a uniform color to the fabric, but also makes it wash durable antibacterial and UV protective.

2. Materials and Methods

2.1 Materials

Cotton fabric (ends per inch/picks per inch= 140/72, gsm=160) was supplied by M/s Vardhman Textiles, H.P. (India). Copper sulphate pentahydrate ($CuSO_4.5H_2O$) was purchased from Merck Pvt. Ltd., Mumbai. Sodium hydroxide was analytical grade. Deionized (DI) water was used in preparation of all solutions.

2.2 Method of deposition of copper oxide on fabric

The scoured and bleached cotton fabric was washed with 1 g/L nonionic detergent to remove the dirt and any other impurity on it. It was rinsed and dried at room temperature.

A transparent solution of 4% copper sulphate pentahydrate precursor ($CuSO_4.5H_2O$) was prepared in 100 ml of water and the untreated cotton fabric was introduced in the solution. The temperature of the solution was gradually raised to 80 ^{0} C in 60 min with gentle stirring. Now, a 2% solution of sodium hydroxide was added drop-wise eventually to raise the pH upto 6. The heating was further continued for 30 min at boil. The treated fabric was soaped, rinsed and dried in hot air oven at 50 ^{0} C. Similar treatment was carried out using higher concentrations of precursor, i.e. 6% and 8% to compare the results. The untreated cotton fabric is named as sample U. The copper oxide coated fabric samples, prepared by using precursor concentrations of 4%, 6% and 8% have been represented as sample A, B and C respectively.

2.3 Characterization methods

The morphology of deposition of copper oxide thin coating on cotton fabric surface was examined using scanning electron microscope (SEM), EVO 50, Carl Zeiss AG, Germany (2006). The physical appearance of the fabrics was recorded in the form of their photographic images. Inductively Coupled Plasma- Mass Spectroscopy (ICP-MS) was used to measure the amount of copper (Cu) in fabric after treatment. This characterization was done by ICP-MS system, Agilent 7900. In this case, a microwave-assisted acidic digester first digests a known amount of fabric sample at 300 ^{0} C. Spectral interferences originated due to the presence of any other component in the samples were identified and removed. Eventually, the amount of Cu in the sample was determined in terms of parts per million (ppm) of the sample.

The treated samples were washed to monitor the possibility of any change in the properties after treatment. Washing was carried out as per ISO 105 C10: 2006 – B, using laundro-meter at 50 ^{0}C temperature in presence of 5 g/L of soap. The material to liquor ratio was kept as 50:1. The evaluation of the UV protection property and antibacterial activity of the treated samples was carried out after 5 standard washes to observe the wash durability of the treatment.

2.4 Testing methods

UV protection property of the fabrics was evaluated out using UV-visible spectrophotometer (UV-2000F, labsphere, USA). The diffuse transmittance of all the samples in the wavelength range of 250 – 450 nm was measured using this instrument. On the basis of recorded data, UV protection factor (UPF) of the fabric was calculated as per AATCC 183:2010 standards. UPF is the ratio of average effective UV irradiance transmitted through air to the average effective UV irradiance transmitted through the fabric using the formula given below:

$$\mathbf{UPF} = \frac{\sum_{290}^{400} E(\lambda).\ \varepsilon(\lambda).\ \Delta(\lambda)}{\sum_{290}^{400} E(\lambda).\ \varepsilon(\lambda).\ T(\lambda).\ \Delta(\lambda)}$$

where,
E(λ) = relative erythemal spectral effectiveness;

$\varepsilon(\lambda)$ = solar spectral irradiance (W m^{-2} nm^{-1});
$T(\lambda)$ = average of measured spectral transmittance of the sample (%);
$\Delta(\lambda)$ = measured wavelength interval (nm);

The antibacterial property of the treated samples was examined against gram positive bacteria *S. aureus* using zone of inhibition method. It is a quick way to assess the antibacterial activity of any material to the targeted bacteria. In this method, the incubated culture of *S. aureus* mother culture was first examined with respect to its absorbance value to be in the range of 0.08 – 0.1 units. 200μl of the suspension of mother culture was taken and spread over the agar plates. The treated fabric were then placed on inoculated medium and further incubated for next 24 h at 37°C to allow a controlled bacterial growth. The zone of inhibition was then observed. The size of the inhibited zone is an indicative of the efficacy of the specific antibacterial agent contained within the treated sample.

Air permeability, tensile strength and crease recovery angle of the fabrics were evaluated before and after the treatment. The tensile strength in the warp direction of the fabrics was measured in Instron universal tester (model- 3365) following ASTM standard D5035–11 and the effect of treatment on tensile strength of fabric was observed. The air permeability value of the fabric was measured in Textest Fx-3300 (Switzerland) under a pressure of 125 Pa as per BS: 5636. The crease recovery angle of fabric was determined by Shirley crease recovery tester.

3. Results & discussion

3.1 Ultraviolet Protection Factor (UPF)

The UPF mean of all the treated fabric samples were measured after their washing. To observe wash durability of the treatment, these UPF values were compared with the each other after 5 consecutive washes. The results are shown in Fig. 1. All the coated fabric samples are giving UPF mean more than 50, as compared to untreated cotton fabric (UPF mean = 7.1). As the concentration of precursor is raised in sample A to C, the deposition of copper oxide on fabric increases and UPF values also goes up gradually (UPF value increases from 58.4 in sample A to 90.5 in sample C). Even after 5 consecutive washes, the UPF values do not go down below 50 in any of the treated samples, which indicate the treatment to be wash durable.

Sample code	UPF Value	
	After 1st wash	After 5 washes
U	7.2 (±0.4)	7.1 (±0.3)
A	58.4 (±3.6)	51.2 (±4.8)
B	72.9 (±5.4)	66.8 (±3.3)
C	90.5 (±6.9)	85.7 (±4.1)

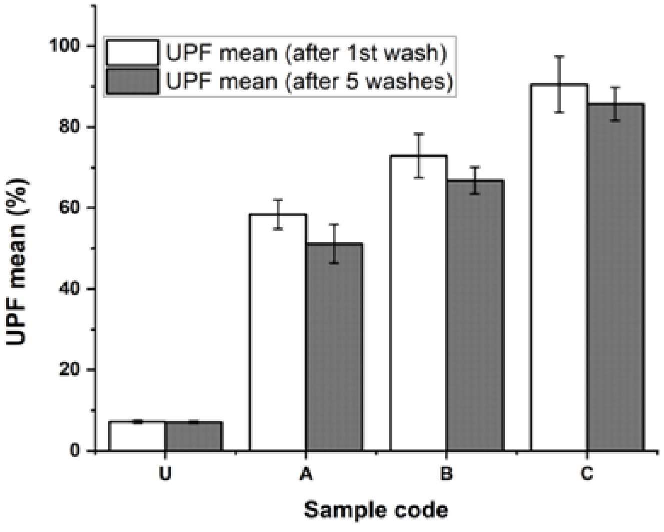

Figure 1- UPF mean of copper oxide coated fabric

3.2 Evaluation of antibacterial property

The results of antibacterial testing using zone of inhibition method (AATCC 143) have been compared between sample U and sample C as shown in Figure 2. In the petridish containing untreated cotton fabric (sample U), as expected no zone of inhibition was found. Unlike this, the treated sample C has shown a distinct zone of inhibition for Gram positive bacteria (*S.aureus)*. With gradual increase in the deposition level of copper oxide, the diameter of bacteria inhibition also increses gradually. The antibacterial result depends on the releasing capability and ion-exchange property of the fabric containing varying amount of copper oxide on it. The tiny particles of copper oxide on fabric react with the cell wall of bacteria through endocytosis mechanism and the ions are released in the bacterial cells [18].

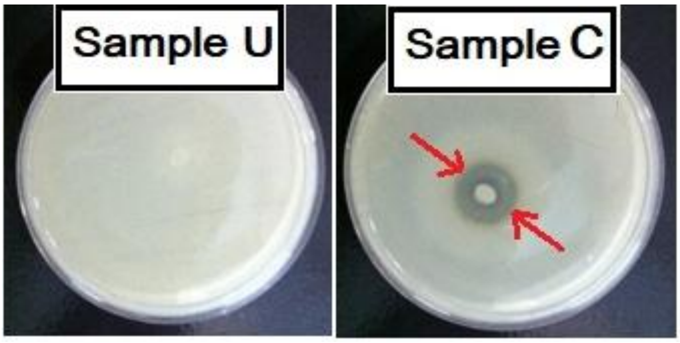

Figure 2- Images of zone of inhibition of untreated and copper oxide treated fabric (Against *Gram positive bacteria*)

3.3 Surface morphology and appearance

SEM study was carried out to observe the changes in the surface morphology of cotton fabric after the treatment. As can be seen in Figure 3, unlike untreated cotton (sample U), there is a deposition of copper oxide tiny particles of size less than 200 nm in treated fabric (sample C). At some places, the deposition of copper oxide is in the form of a very thin layer is also observed. However, overall the deposition is uniform. To have an idea of the samples prepared in this way, the scanned photographic images of untreated and copper oxide coated fabric samples of varying concentration have been shown in Figure 4. As reflected in the images, the color of the fabrics after treatment was found to be uniformly distributed within the surface.

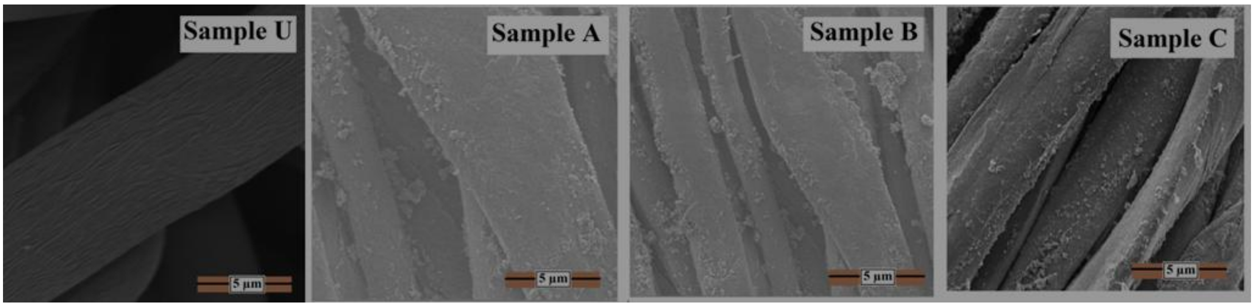

Figure 3 - SEM images of copper oxide coated cotton fabric

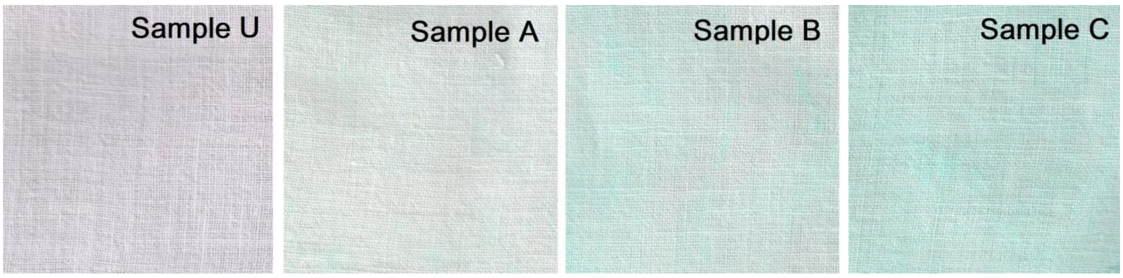

Figure 4- Photographic images of untreated and copper oxide treated fabric samples

3.4 Measurement of copper content in fabric

ICP-MS analysis was carried out to measure the content of copper deposited on fabric in the form of its oxide. As reported in Table 1, the content of copper in fabric was found to be around 435, 492 and 521 ppm in sample A, B and C respectively after 1st wash. On consecutive 5 washing cycles, however a little reduction in the ppm level of all the samples was observed as given in table.

Table 1- Content of Copper in samples after wash

Sample code	Content of Copper (ppm) (after 1st wash)	Content of Copper (ppm) (after 5th wash)
U	--	--
A	435	404
B	492	451
C	521	486

3.5 Evaluation of physical properties of the fabric samples

Air permeability, tensile strength and crease recovery angle properties of untreated and copper oxide coated cotton fabrics were evaluated and recorded in Table 2. All the samples were subjected to a standard wash before the measurement of these properties. As can be observed in the Table 1, the air permeability values of treated fabrics are slightly lower than untreated fabric. This might have happened due to the coating of copper oxide on the fabric surface. As the concentration of precursor in the treatment bath increases, the air permeability value of the treated fabric gradually decreases. The highest value for air permeability has been observed in cotton fabric without any treatment.

The tensile strength of all the samples was measured in warp-wise direction and the average value of strength (in Kgf) is represented in Table 2. There is a small reduction (2-7%) in the tensile strength of copper oxide treated samples with respect to the untreated sample (sample A, B, C vs. sample U), although this reduction is not considerable. The small reduction in the tensile strength after treatment may be due to the acidic pH conditions of treatment at boil.

The crease recovery angle of the fabrics after the coating slightly goes down as compared to the untreated fabric. This shows that fabrics become marginally stiffer after the impregnation of copper oxide.

Table 2 - Air Permeability, Tensile Strength and Crease Recovery Angle of untreated and copper oxide treated cotton fabrics

Sample code	Air Permeability Value	Tensile Strength (Kgf)	Crease Recovery Angle (^{0})
U	8.67	37.62	86.2
A	8.32	36.87	78.9
B	8.15	36.05	75.1
C	7.98	35.60	73.4

4. Conclusions

Cotton fabric was successfully coated with copper oxide on its surface using a simple chemical reduction method. The thin coating was distributed on fabric in the form of tiny particles. This copper oxide coating on fabric not only gives a bright sea green color to the fabric but also imparts a wash durable UV protection property. The treated fabrics also exhibited antibacterial behavior against Gram-positive bacteria as determined by zone inhibition method. No considerable decrement in physical properties of fabric was observed after the treatment. However, there was a small reduction found in the tensile strength and air permeability values of the treated samples. Hence, this cost effective method can be used to introduce multi-functionalities in textile substrates.

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